End of Fiscal Year Letter
Third Year of Contract N00014-89-J-1238

A Study of the Gas-phase Chemistry of Solid Propellant Ingredients Using CO_2 Laser Heating

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The Pennsylvania State University

INTRODUCTION

This research program is designed to address the critical need for data on the gas-phase chemistry of solid propellants through the development and application of a Microprobe Mass Spectrometer (MPMS) system. The MPMS system is being used to study the gas-phase chemistry occurring above solid propellant ingredients and actual solid propellants when they are heated and/or ignited by the heat flux from a CO_2 laser. Currently the MPMS system uses quartz microprobes with orifice sizes of twenty microns which result in a spatial resolution of approximately 100 microns. In addition to the MPMS system, direct and Schlieren photography are being used to study the flame structure and twenty-five micron thermocouples are being used to measure the gas-phase temperature profile.

The specific goal of this research is to obtain detailed species profiles of the major reacting species above the surface of individual propellant ingredients and actual propellants in order to obtain an improved understanding of the controlling chemical processes and of the interactions of binders and oxidizers in heterogeneous propellants. In the testing both heterogeneous and homogeneous propellants are being studied as well as their individual ingredients. Testing to date has included RDX, HTPB, BAMO/NMMO, XM-39 and BLX-9, which are RDX based materials, and finally M-10 and JA-2, which are double-base propellants.

ENHANCEMENTS OF THE MPMS SYSTEM

During the last year several significant enhancements of the MPMS system capabilities were made. After considerable development work diatomic hydrogen was detected with the system. This capability is a significant because other measurement techniques including PLIF and FTIR cannot measure hydrogen, which is present in significant quantities and is potentially an important reactant. Secondly, calibrations for most of the major intermediate species have been performed so that the mole fraction of the various compounds can be determined. Calibrations for many species including H_2, CO, CO_2, NO and NO_2 were performed directly in the gas-phase, then calibration factors for other key species were calculated using these results and data on ionization cross-sections. Finally, new control and data reduction programs were written for the mass spectrometer which have improved the flexibility of the MPMS and the reliability of the data reduction process.

EXPERIMENTAL RESULTS

Over the course of the last year nearly fifty tests were performed with pure RDX and various propellants. For the purposes of illustration of typical results, data from RDX tests will be discussed as well as from JA-2 which is a triple base material.

The RDX results, presented in Figure 1, contain the major species detected for a test of pure RDX in argon at one atmosphere pressure. For this test the laser heat flux was 100 W/cm^2. The probe was placed on the sample surface at the beginning of the test in an attempt to sample gases within the melt layer. The distances presented in the figure are derived from high-speed Schlieren movies which had a spatial resolution of 67 microns.

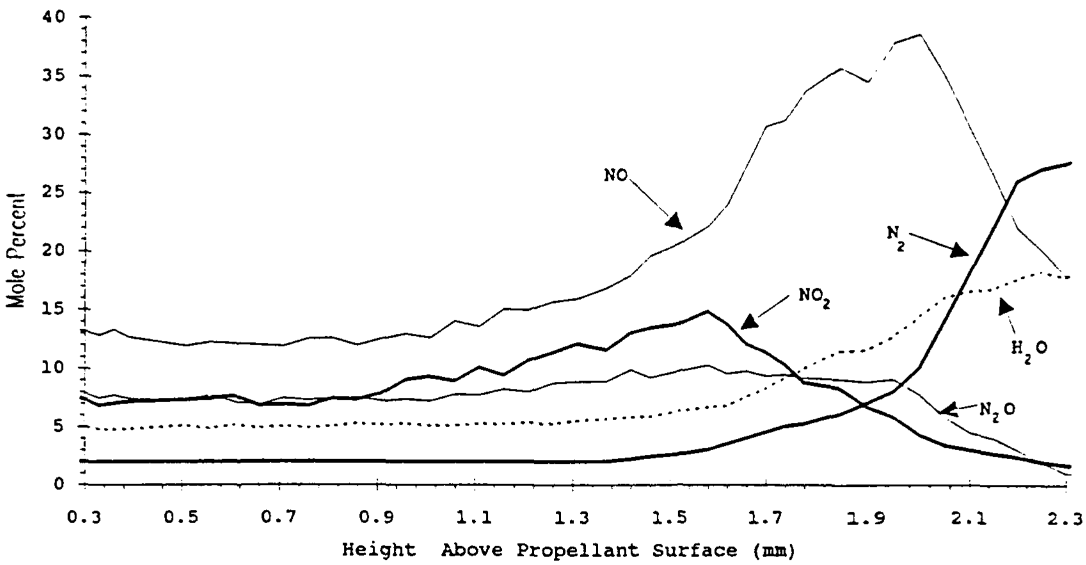
Upon initiation of laser heating a high density region evolves from the surface of the RDX and it is within this region that the high concentrations of formaldehyde are detected. The length of this region as indicated by the figure may be overestimated due to the fact that some of the melted material actually stuck to the microprobe and may have artificially lengthened the time during which species from this region were detected. As the probe leaves this region a rapid rise in NO, CO and HCN occurs as NO and formaldehyde decrease. This region is then followed by a decrease in HCN and NO and a rise in N_2 in the primary flame zone. In these figures then the primary flame appears to occur at a distance of approximately 2mm above the sample surface. This distance is somewhat larger than expected; two possible reasons are the effect of the incident heat flux and the effect of the melt layer material which was mentioned above.

When the above results are compared to the results of Korobeinichev, et al., the comparison is quite good for the region above the melt layer, i.e., the true gas-phase region. Trends in species profiles are the same and the concentrations of the species are comparable, especially considering the fact that the data from Korobeinichev was obtained at 0.5 atmospheres without any external heat flux.

Representative results for a double-base propellant, in this case JA-2, are presented in Figure 2. These results were obtained in tests performed in a similar manner to the RDX test with the probe initially located on the sample surface; the ambient gas was argon at one atmosphere pressure and the heat flux was 100 W/cm^2. In these results the initial data taken within approximately one millimeter of the surface occurs during the ignition transient; the remainder of the data is taken from the dark zone. The major species identified include NO, CO, CO_2, H_2O and H_2 and they all show rather gradual changes within the dark zone. Minor species include HCN, NO_2 and formaldehyde. Due to the arrangement of the sample and the microprobe, species from within the fizz zone could not be sampled. However, some of the species that feed the primary flame are measured during the transient period of the test. Overall these results are in good agreement with prior studies in terms of the species detected in the dark zone; however, since they are the first measurements of species profiles, no comparisons of the profiles to earlier work can be performed.

FUTURE WORK

In the next year the work will emphasize nitramine materials and heterogeneous propellants. In particular additional tests with RDX and XM-39 will be performed at different heat fluxes and pressures from 0.5 to 2 atmospheres. Also, if a source of polycyclic nitramine pellets can be found these new materials will also be tested.



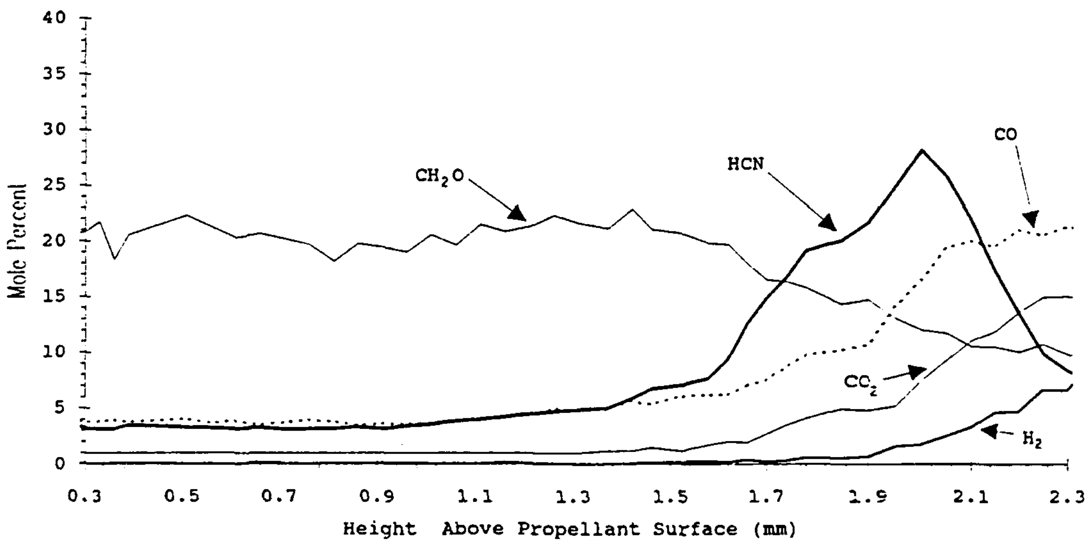


Figure 1. Species profiles for the combustion of RDX in argon at one atmosphere with a heat flux of 100 W/cm^2.

Statement A per telecon Dr. Richard Miller
ONR/Code 1132
Arlington, Va 22217-5000

NWW 2/10/92

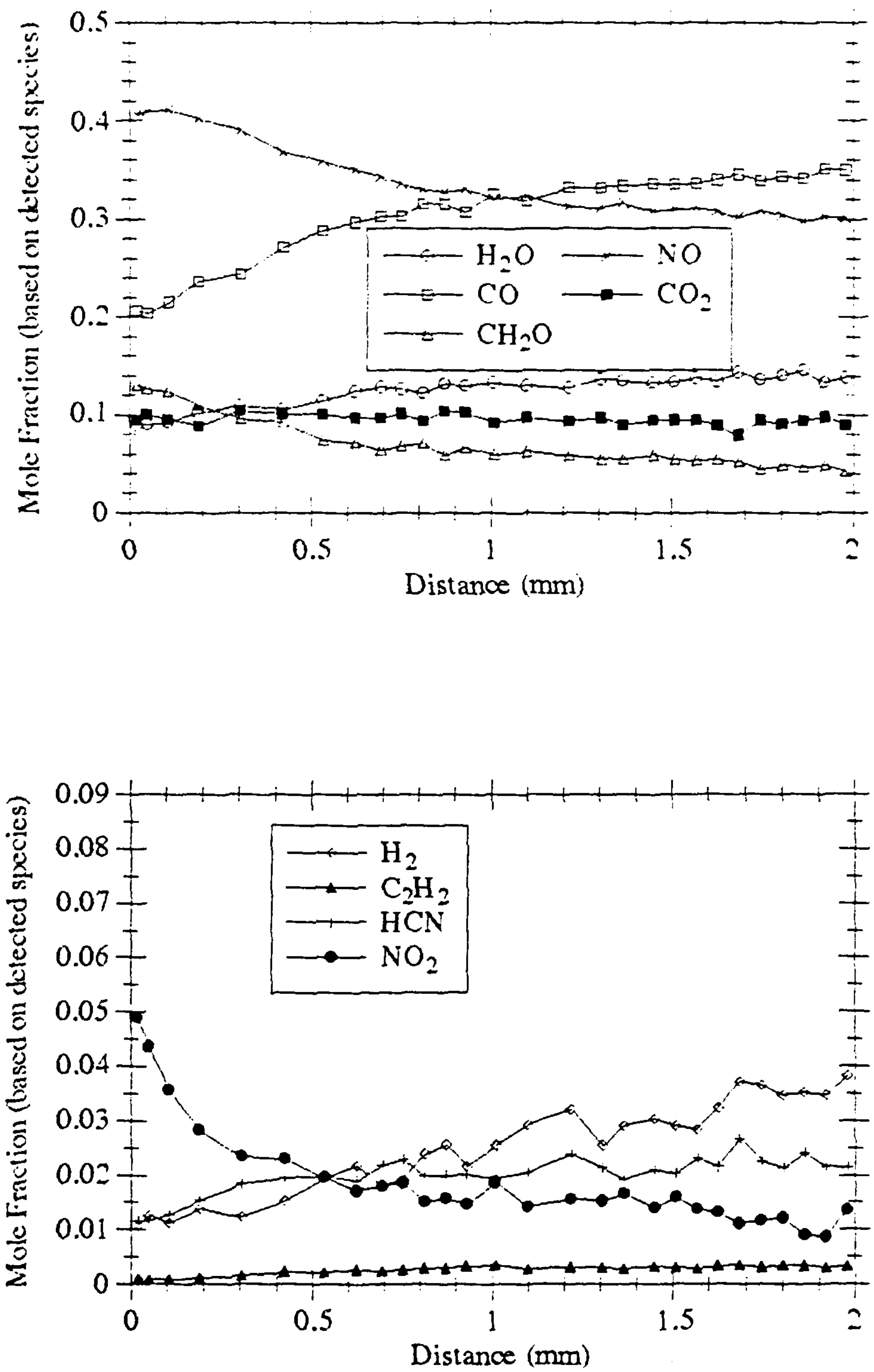


Figure 2. Species profiles for a double-base propellant, JA-2, in argon at one atmosphere with a heat flux of 100 W/cm^2.

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
1 October 1990 through 30 September 1991

R&T Number: (N00014-89-J-1238) 4326821

Contract/Grant Title: A Study of the Gas Phase Chemistry of Solid Propellant Ingredients Using CO_2 Laser Heating

Scientific Officer: Dr. R. S. Miller

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a. Number of Papers Submitted to Referred Journal but not yet published: 3

b. Number of Papers Published in Referred Journals: (List Attached): 5

c. Number of Books or Chapters Submitted but not yet Published: 0

d. Number of Books or Chapters Published (List Attached): 0

e. Number of Printed Technical Reports & Non-Referred Papers (List Attached): 0

f. Number of Patents Filed: 0

g. Number of Patents Granted (List Attached): 0

h. Number of Invited Presentations at Workshops or Professional Society Meeting (List Attached): 0

i. Number of Presentations at Workshops or Professional Society Meetings (List Attached): 5

j. Honors/Awards/Prizes for Contract/Grant Employees: (List Attached, may include Society Awards/Offices, Promotions, Faculty Awards/Offices, etc.) 1

k. Providing the following information will assist with statistical purposes.

PI/CO-PI:	TOTAL	1	Grad Students:**	TOTAL	2
	Female	0		Female	0
	Minority*	0		Minority*	0

Post Doc:**	TOTAL	0
	Female	0
	Minority*	0

l. Degrees Granted (List Attached): 4

* Underrepresented or minority groups include Blacks, Hispanics, and Native Americans.
  Asians are not considered an underrepresented or minority group in science and engineering.

** Supported at least 25% this year on contract/grant.

Enclosure(1)

LIST OF PUBLICATIONS/REPORTS/PATENTS/GRADUATES

1. Papers Published in Referred Journals:

Palumbo, J. H. and T. A. Litzinger. The Effects of Hydrotreatment of Coal-Derived Synthetic Fuels on DI Diesel Emissions and Performance. SAE Transactions, J. of Fuels and Lubricants, Vol. 98, pp. 1179-1189 (1990).

Flanigan, C. T., T. A. Litzinger and R. L. Graves (Martin Marietta). The Effect of Aromatics and Cycloparaffins on DI Diesel Emissions. SAE Transactions, J. of Fuels and Lubricants, Vol. 98, pp. 1166-1178 (1990).

Litzinger, T. A. A Review of Experimental Studies of Knock Chemistry in Engines. Prog. in Energy and Comb. Sci., Vol. 16, pp. 155-167 (1990).

Hoffman, J., W. Lee, T. A. Litzinger, D. A. Santavicca and W. J. Pitz. The Oxidation of Propane at Elevated Pressures - Experiments and Modelling. Combustion Science and Technology, Vol. 77, pp. 95-125 (1991).

Chen, D. M., W. H. Hsieh, T. S. Snyder, V. Yang, T. A. Litzinger and K. K. Kuo. Combustion Behavior and Thermophysical Properties of Metal Based Solid Fuels. AIAA J. of Propulsion and Power, Vol. 7, pp. 250-257 (1991).

2. Books (and sections thereof) Published:

None

3. Technical Report, Non-Refereed Papers:

None

4. Presentations:

Solbrig, C. E. and T. A. Litzinger. The Effect of Intake Charge Temperature on Combustion and Emissions in an Optically Accessible Engine With and Without Swirl. SAE International Fuels and Lubricants Meeting, Tulsa, OK, Paper No. 902060 (Oct. 1990).

Lee, W., C. E. Solbrig, T. A. Litzinger and R. J. Santoro. Planar Laser Light Scattering for the In-Cylinder Study of Soot in a Diesel Engine. SAE International Fuels and Lubricants Meeting, Tulsa, OK, Paper No. 902125 (Oct. 1990).

Espey, C., J. A. Pinson and T. A. Litzinger. Swirl Effects on Mixing and Flame Evolution in a Research DI Diesel Engine. SAE International Fuels and Lubricants Meeting, Tulsa, OK, Paper No. 902076 (Oct. 1990).

Litzinger, T. A., W. A. Riggs, J. Papciak and E. Ritchey. Conditions at the Intake Valve of a Spark Ignition Engine. A.C.S. Meeting, Atlanta, GA (April 1991).

Lee, W., T. A. Litzinger and R. J. Santoro. The Effect of Swirl on In-Cylinder Soot Evolution in a DI Diesel Engine. Fall Technical Meeting of the Eastern Section of The Combustion Institute, Orlando, FL, 4 pp. (Dec. 1990).

5. Patents Granted:

None

6. Degrees Granted (name, date, degree):

James S. Hoffman	8/91	Ph.D.
Charles E. Solbrig	5/91	M.S.
William A. Riggs	8/91	M.S.
William L. Mitchell	8/91	M.S.

LIST OF AWARDS/HONORS/PRIZES

Name of Person Receiving Award	Recipient's Institution	Name of Award	Sponsor of Award
T. A. Litzinger	Penn State Univeristy	Excellence in Oral Presentation	Society of Automotive Engineers

Enclosure (3)

OTHER SPONSORED RESEARCH

(Include title, sponsors's name, dollar amount and start and end dates for the award)

Research on Diesel Engine Emissions
Mobil Oil Company
$40,000 (7/86-6/91)

Presidential Young Investigator Award
National Science Foundation
$312,000 (7/87-6/92)

Soot Transport in a DI Diesel Engine
Cummins Engine Company
$168,500 (6/87-5/92)

An In-Cylinder Investigation of Soot and NO Formation in a Direct Injection Diesel Engine
U.S. Department of Energy
$605,000 (7/91-6/94)

Conditions at the Intake Valve of an Operating SI Engine
Texaco Research Center
$180,000 (8/88-12/92)

Enhancement of Methanol Combustion in Heavy Duty Engines Using In-Cylinder Catalysts
Martin-Marietta Energy Systems
$143,739 (7/89-10/91)